PCT/GB98/00705

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The Patent Office

09/380864

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REC'D 20 MAY 1998
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Dated 2 April 1998

Form 1/77

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1/77

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P01/7700 25.00

# Request for grant of a patent

*(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)*

**The Patent Office**

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

AA 1335 GB

2. Patent application number
*(The Patent Office will fill in this part)*

**9705010.8** 10 MAR 1997

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

JOHNSON MATTHEY PUBLIC LIMITED COMPANY
78 HATTON GARDEN, LONDON EC1N 8JP, UK

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

5362608005

4. Title of the invention

IMPROVEMENTS IN EMISSIONS CONTROL SYSTEMS

5. Name of your agent *(if you have one)*

L S BREWER

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

JOHNSON MATTHEY TECHNOLOGY CENTRE
BLOUNTS COURT, SONNING COMMON,
READING RG4 9NH

Patents ADP number *(if you know it)*

5609060001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

| Country | Priority application number *(if you know it)* | Date of filing *(day / month / year)* |
|---|---|---|
| | | |

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

| Number of earlier application | Date of filing *(day / month / year)* |
|---|---|
| | |

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
*a) any applicant named in part 3 is not an inventor, or*
*b) there is an inventor who is not named as an applicant, or*
*c) any named applicant is a corporate body.*
*See note (d))*

YES

**Patents Form 1/77**

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

| | |
|---|---|
| Continuation sheets of this form | 0 |
| Description | 9 |
| Claim(s) | 2 |
| Abstract | 0 |
| Drawing(s) | 0 |

10. If you are also filing any of the following, state how many against each item.

| | |
|---|---|
| Priority documents | |
| Translations of priority documents | |
| Statement of inventorship and right to grant of a patent *(Patents Form 7/77)* | |
| Request for preliminary examination and search *(Patents Form 9/77)* | 1 |
| Request for substantive examination *(Patents Form 10/77)* | |
| Any other documents *(please specify)* | |

11. I/We request the grant of a patent on the basis of this application.

Signature L S Brewer Date 10 MARCH 1997

L S BREWER

12. Name and daytime telephone number of person to contact in the United Kingdom

MRS F E STRANGE 0118 924 2125

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**Notes**

a) *If you need help to fill in this form or you have any questions,* [redacted] *space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*

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same conditions, a % carbon monoxide conversion of usually greater than 70%, preferably greater than 80%, especially greater than 90%, particularly greater than 95%. Defining the catalyst systems according to measurement under these conditions does not mean of course that they are necessarily operated under these conditions. In a particular embodiment, the first catalyst system is such that the exhaust gases from the engine flow over it at a low space velocity, particularly below 40000hr$^{-1}$. The second catalyst system is usually such that the exhaust gases from the engine flow over it at a space velocity of 40000-80000hr$^{-1}$. The first catalyst system usually contains platinum. The second catalyst system usually contains platinum. Thus, in a particular embodiment each contains platinum. For use, the first catalyst system can be mounted ahead of the second catalyst system in the exhaust apparatus of the engine. The present engine is preferably in a vehicle, for example a passenger car or heavy duty truck.

The skilled person may apply the present invention in a variety of ways. The first catalyst system may be, for example, a relatively low loading of catalytically active component on a substrate, optionally in combination with components that can retain NOx and/or reducing species, such as zeolite or like absorbents, or alkaline earth metal compounds. We have discovered that reducing the loading of catalytically active component (usually comprising platinum group metal, especially platinum and/or palladium and/or rhodium, particularly platinum, optionally in the presence of base metal components) compared to conventional exhaust gas catalysts, serves to increase the selectivity of the catalyst system towards NOx reduction.

In a particular embodiment, the first catalyst system provides a low space velocity. Normal space velocities for exhaust catalysts systems are 40000-80000hr$^{-1}$. A lower space velocity may be achieved readily in practice by increasing the volume of the catalyst, or by utilising two catalyst "bricks" in parallel.

The second catalyst system is required to be of high oxidation activity. Such catalyst need not have NOx selectivity, but must be capable of oxidising hydrocarbons and carbon monoxide under the reaction conditions, to the desired extent, usually so as to satisfy emission standards regulations. Normal space velocities may be used. A suitable oxidation catalyst comprises platinum on a high surface area support, optionally with other components which promote such oxidations.

The skilled person is very familiar with conventional exhaust gas catalyst technology. Generally, a support which is a honeycomb-type extruded ceramic or wound metal monolith or "brick" is coated with a surface area-enlarging washcoat, for example a washcoat consisting of or comprising alumina. Deposited onto the washcoat is a coating of one or more catalytic components, optionally with one or more other components such as ceria, zirconia, zeolite or the like, and the catalyst may be multi-component deposited in discrete layers or some components may be layered, with other components distributed throughout such layers. In the present invention, the actual catalysts chosen, and their construction, are not critical providing they meet the criteria

**AA 1335**

# IMPROVEMENTS IN EMISSIONS CONTROL SYSTEMS

This invention concerns improvements in emissions control systems, and more especially it concerns improvements in emissions control for engines operating at lean air/fuel ratios.

It will be appreciated that with lean-burn engines of various types, including particularly diesel, lean-burn gasoline and direct injection gasoline engines, the control of NOx tends to be difficult. This is understandable in that the exhaust gases contain relatively high amounts of oxygen and hence the removal of NOx involves reduction of NOx to $N_2$ in an overall oxidising atmosphere. Prior proposals have involved storage of NOx in the emission control system until a time when the exhaust gas contains relatively less oxygen, that is until the engine is running "rich", *eg* during

acceleration. Another proposal is to store unburnt hydrocarbon until a point at which it can be released to contribute to NOx reduction. There remains the need, however, for yet further systems and strategies to achieve control of NOx emissions under lean conditions.

The present invention provides a novel emission control system for a lean-burn internal combustion engine, comprising a first catalyst system having relatively high selectivity for NOx reduction, and a second catalyst system having high activity for the oxidation of hydrocarbons and carbon monoxide.

The invention also provides a process for the control of emissions from a lean-burn internal combustion engine, comprising passing the exhaust from the engine over a first catalyst system having relatively high selectivity for NOx reduction, then passing the product gases exiting from said first catalyst system over a second catalyst system having high activity for the oxidation of hydrocarbons and carbon monoxide.

By selectivity for NOx reduction is meant the ratio of %NOx conversion to % hydrocarbon conversion. The catalyst system having relatively high such selectivity usually has a selectivity of at least 0.2, preferably at least 0.3, especially at least 0.4; this is as measured at a temperature of 230°C, a space velocity of 25000hr$^{-1}$ and a hydrocarbon:NOx input ratio of 3:1 counting the [redacted] monoxide has, as measured under the same conditions, a % hydrocarbon conversion of usually greater than 80%, preferably greater than 90%; it has, as measured under the

It is now well established that carbon monoxide and hydrocarbons play a part in the reduction of NOx. For example, taking the hydrocarbon as $C_3H_6$, the following reactions could take place:

$$18NO + 2C_3H_6 \rightarrow 9N_2 + 6CO_2 + 6H_2O$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

The molar ratios required for NOx reduction, namely $C_3H_6$ to NO and CO to NO, are exceeded over the European test cycle <u>on average</u> with a diesel engine. However, there is competition between NOx and oxygen for the reducing species, and normally only quite low NOx conversions, (*eg* much less than 10%) are achieved in the European test cycle.

It may be preferred to increase NOx conversion under certain conditions by increasing the relative quantity of hydrocarbons in the exhaust. For example, injection of fuel into the exhaust upstream of the first catalyst system may be used. Alternatively, HC storage using zeolites or the like, may be useful. It will be appreciated that there would be a small fuel consumption penalty if fuel injection into the exhaust is used. The high activity second catalyst system is readily capable of catalysing the oxidation of any excess hydrocarbons under the lean conditions.

Conventional catalyst manufacturing technology may be used.

The first and second catalyst systems may be mounted in a single "can" in the exhaust system, or they may be separated by a length of exhaust pipe.

The present invention is illustrated by the following Tests.

**Test 1**

The increase of NOx selectivity corresponding to decreasing platinum loading was shown for a standard 6in (15.2cm) catalyst brick. Exhaust from a 1.9 litre turbo direct injection diesel bench engine, operating at steady state conditions was used. NOx selectivity is measured as % NOx conversion at 230°C/% hydrocarbon conversion at 230°C. The results are shown in Table 1 below.

**TABLE 1**

| Pt loading (g/$ft^3$) | NOx selectivity at 230°C |
|---|---|
| 10 | 1.00 |
| 25 | 0.40 |
| 50 | 0.34 |
| 75 | 0.33 |
| 100 | 0.31 |

A reduced loading of catalyst therefore improves selectivity.

**Test 2**

The increase in NOx conversion, at a constant platinum loading (1.5g) *per* catalyst brick, by decreasing space velocity and reducing loading in g/unit volume was measured. The same engine and conditions was used as in Test 1. The NOx conversion was measured with "raw" exhaust from the engine ("Passive") and with the addition of hydrocarbon into the exhaust to yield a HC3:NOx ratio of 2.0:1. HC3 means that the hydrocarbon is counted as equivalent propane.

**TABLE 2**

| Catalyst length (inches) | Maximum NOx Conversion (%) | |
|---|---|---|
| | Passive | Added HC |
| 1 | 6 | 13 |
| 2 | 12 | 17 |
| 3 | 16 | 22 |
| 4 | 18 | 25 |
| 5 | 22 | 29 |
| 6 | 25 | 33 |

It can clearly be seen that increasing catalyst length and hence decreasing space velocity is beneficial in overall NOx conversion.

## EXAMPLE 1

A 1996 model passenger car with a 2.5 litre turbo direct injection diesel engine was used with several different exhaust catalyst systems, for standard EUDC emission tests (Extra Urban Driving Cycle emission tests of the European Union). The results are shown in Table 3 below.

### TABLE 3

**Catalyst System**

| | HC | CO | NOx | HC+ NOx | PM (4) | %NOx |
|---|---|---|---|---|---|---|
| No Catalyst | 0.322 | 1.034 | 0.394 | 0.715 | 0.089 | 0.0 |
| OEM Catalyst (1) | 0.196 | 0.913 | 0.389 | 0.585 | 0.081 | 1.3 |
| New Catalyst (2) | 0.067 | 0.336 | 0.332 | 0.399 | 0.079 | 15.7 |
| Lean-NOx Catalyst (3) | 0.054 | 0.495 | 0.294 | 0.347 | 0.073 | 25.4 |
| Lean-NOx Catalyst + Oxidation Catalyst (5) | 0.037 | 0.237 | 0.292 | 0.329 | 0.077 | 25.9 |

Notes:

(1) OEM (Original Equipment Manufacturer) catalyst, 6in long, with 46g/ft$^{-3}$ Pt.

(2) Advanced oxidation catalyst, 6 in long with 40g/ft$^{-3}$ Pt.

(3) Lean-NOx catalyst, 12 in long, with 25g/ft$^{-3}$ Pt

[redacted]

(5) Lean-NOx catalyst, 9in long, with 25g/ft$^{-3}$ Pt, followed by oxidation catalyst, 3in long, with 100g/ft$^{-3}$ Pt.

All the catalysts used were fresh, *ie* without ageing.

It can readily be seen that the low loading, low space velocity Lean-NOx Catalyst is very effective in converting NOx, and that the combination according to the invention is remarkably effective.

## CLAIMS

1. An emission control system for a lean-burn internal combustion engine, comprising (A) a first catalyst system, which has a ratio of % NOx conversion to % hydrocarbon conversion of at least 0.2 as measured at a temperature of 230°C, a space velocity of 25000hr$^{-1}$ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane, and (B) a second catalyst system, which has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80% and a % carbon monoxide conversion of greater than 70%.

2. A control system according to claim 1, wherein the first catalyst system is such that the exhaust gases from the engine flow over it at a space velocity below 40000hr$^{-1}$.

3. A control system according to claim 1 or 2, wherein the second catalyst system is such that the exhaust gases from the engine flow over it at a space velocity of 40000-80000hr$^{-1}$.

4. A control system according to any one of the preceding claims, wherein the first catalyst system and the second catalyst system each contains platinum.

[redacted] the preceding claims, wherein the first catalyst system is ahead of the second catalyst system in the exhaust apparatus of the engine.

6. A process for the control of emissions from a lean-burn internal combustion engine, comprising passing exhaust gases from the engine over a first catalyst system, which has a ratio of % NOx conversion to % hydrocarbon conversion of at least 0.2 as measured at a temperature of 230°C, a space velocity of 25000hr$^{-1}$ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane, then passing the product gases exiting from the first catalyst system over a second catalyst system, which has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80% and a % carbon monoxide conversion of greater than 70%.

7. A process according to claim 6, wherein the gases are passed over the first catalyst system at a space velocity below 40000hr$^{-1}$.

8. A process according to claim 6 or 7, wherein the gases are passed over the second catalyst system at a space velocity of 40000-80000hr$^{-1}$.

9. A process according to any one of claims 6-8, wherein the first catalyst and the second catalyst system each contains platinum.

10. A process according to any one of claims 6-9, wherein the engine is in a vehicle.

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JOHNSON MATTHEY

09 MARCH 1998